Food Chemistry 119 (2010) 513–517

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

New diarylheptanoids from the rhizome of *Alpinia officinarum* Hance

Ning An [a,b], Hong-wu Zhang [a], Li-zhen Xu [a], Shi-lin Yang [a], Zhong-mei Zou [a,*]

[a] Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100193, PR China
[b] National Institute for the Control of Pharmaceutical and Biological Products, Beijing 100050, PR China

ARTICLE INFO

Article history:
Received 8 April 2009
Received in revised form 2 June 2009
Accepted 23 June 2009

Keywords:
Galangal
Alpinia officinarum Hance
Diarylheptanoids
Officinaruminane A
Officinaruminane B
5(S)-Acetoxy-7-(4-dihydroxyphenyl)-1-phenyl-3-heptanone

ABSTRACT

Three diarylheptanoids, officinaruminane A (**1**), officinaruminane B (**2**), 5(S)-acetoxy-7-(4-dihydroxyphenyl)-1-phenyl-3-heptanone (**3**), together with six known ones , (5*R*)-5-hydroxy-1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-3-heptanone (**4**),(5*R*)-5-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4,5-dihydroxy-3-methoxyphenyl)-3-heptanone (**5**), 1-phenyl-7-(4-hydroxy-3-methoxyphenyl)-4-*E*-en-3-heptanone (**6**), 1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-4*E*-en-3-heptanone (**7**), 1-phenyl-7-(4-hydroxyphenyl)- 4*E*- en-3-heptanone (**8**), and 3,6-furan-7-(4′′-hydroxy-3′′-methoxyphenyl)-1-phenylheptane (**9**), were isolated from the rhizomes of *Alpinia officinarum* Hance by column chromatography on silica gel, MPLC and preparative thin-layer chromatography (TLC). The structures of these compounds were elucidated on the basis of mass spectrometry, ^{1}H NMR, ^{13}C NMR, HMQC and HMBC data. Among them, **1** is a diarylheptanoid with a pyridine ring, and 2 is a diarylheptane monoterpene.

1. Introduction

Galangal, the rhizome of *Alpinia officinarum* Hance (Zingiberaceae) is a spice widely used in Europe and China for over 1000 years. It has also been used as a traditional medicine in China for relieving stomach ache, treating colds, invigorating the circulatory system, and reducing swelling (Jiangsu New Medicinal College, 1979) *A. officinarum* Hance is cultivated in the Hainan and Guangdong provinces of China. Of the many chemical constituents isolated from this plant, diarylheptanoids are among the characteristic compounds (Shin, Kinoshita, Koyama, & Takahashi, 2002; Sun et al., 2008), which are known to possess antiplatelet (Doug, Chen, Xu, Kadota, & Namba, 1998; Fan, Kang, Han, & Han, 2007), antioxidative (Yao et al., 2007), antiproliferative (Ali, Tezuka, Banskota, & Kadota, 2001), anti-emetic (Shin et al., 2002), antihepatotoxic (Hikino et al., 1985), anti-inflammatory (Lee, Kim, & Ryu, 2006) inhibition of 5α-reductase (Kim et al., 2003), and inhibition of pancreatic lipase (Shin, Han, Song, Baek, & Kim, 2004) activities. Our continuing study (An et al., 2008; An, Xu, Zou, & Yang, 2006) has led to the isolation of three new diarylheptanoids (**1**–**3**), together with 6 known analogues (**4**–**9**). This paper deals with the isolation and structural elucidation of the new diarylheptanoids.

2. Materials and methods

2.1. Materials

The dried rhizomes of *A. officinarum* Hance were collected in October 2002 from Xu-Wen County, Guangdong province of China and identified by Prof. Shou-Quan Lin, Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, China. A voucher specimen is deposited in the Natural Medicine Research Center of this Institute.

2.2. General procedure

Optical rotations were measured using a JASCO DIP-360 digital polarimeter. UV spectra were conducted on a Philips PYE Unican Pu8800 spectrophotometer. Mass spectra were obtained on a VG ZAB-2f mass spectrometer. NMR spectra were performed using a VARIAN Inova 600 spectrometer. All spectra were acquired in $(CD_3)_2CO$ and chemical shifts are reported in ppm using residual solvent signals (δ_H 2.05 and δ_C 206.7) as reference. The MPLC were performed on a system equipped with a Büchi pump and Büchi columns with normal phase silica gel 60 (15–40 μm, Qingdao Haiyang Chem Co.). Silica gel (200–300 mesh) for CC and GF254 for analytical TLC were purchased from the Qingdao Marine Chemical Factory, China.

* Corresponding author. Tel./fax: +86 10 62899756.
E-mail address: zmzou@implad.ac.cn (Z.-m. Zou).

0308-8146/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2009.06.046

2.3. Extraction and isolation

The dried rhizomes of *A. officinarum* Hance (28 kg) were extracted three times with 95% EtOH (170 l) at room temperature. After evaporation of EtOH *in vacuo*, the residue (2.2 kg) was suspended in H_2O and extracted with petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH, respectively. The $CHCl_3$ extract (350 g) was subjected to column chromatography over silica gel eluted with a mixture of petroleum ether (60–90 °C)-EtOAc (1:0–0:1) in gradient to give eight fractions (Fr.1–Fr.8). Fr. 3 (16 g) was subjected to column chromatography on silica gel eluted with petroleum ether–EtOAc (98:2–90:10) to afford six sub-fractions (Fr.3.1–3.6). Fr.3.2 (2.7 g) was repeatedly chromatographed over silica gel eluted with petroleum ether–EtOAc (95:5) and purified by preparative TLC (petroleum ether–Me_2CO 6:1) to give **6** (4 mg), **3** (6 mg) and **8** (4 mg). Fr.3.3 (1.6 g) was subjected to MPLC (silica gel H, petroleum ether–Me_2CO 95:5) to yield **9** (3 mg); Fr.3.4 (1.1 g) was separated by preparative TLC [petroleum ether (60–90 °C)-EtOAc (8:2)] to give **1** (5 mg) and **2** (3 mg); Fr.8 (9 g) was subjected to MPLC (silica gel H) eluted with $CHCl_3$–MeOH (98:2–80:20) to give seven subfractions (Fr. 8.1–8.7). Fr.8.2 was subjected to MPLC (silica gel H, petroleum ether–Me_2CO 4:1) to yield **7** (8 mg) and **4** (10 mg). Compound **5** (15 mg) was obtained from Fr.8.3 by MPLC (silica gel H, petroleum ether–Me_2CO 7:3).

2.4. Spectrometric identification of isolated compounds

Officinarumane A **(1),** colourless oil, UV (MeOH) λ_{max} nm: 202, 250 (sh); HREI-MS *m/z*: 551.2823 ($C_{39}H_{37}O_2N$, 551.2824); EIMS *m/z* (%): 551 (M^+, 60), 460 (100), 446 (30), 418 (70), 237 (15), 105 (10), 91 (65); for the ^1H and ^{13}C NMR data see Table 1.

Officinarumane B **(2),** colourless oil, UV (MeOH) λ_{max} nm: 268, 209; HREI-MS *m/z* 400.2767 ($C_{29}H_{36}O$, 400.2766); EIMS *m/z* (%): 400 (M^+, 15), 309 (5), 295 (12), 267 (50), 133 (30), 105 (98), 91 (100); for the ^1H and ^{13}C NMR data see Table 1.

5(S)-acetoxy-7-(4-dihydroxyphenyl)-1-phenyl-3-heptanone **(3),** colourless oil, $[\alpha]_{20}^{D}$ + 5.45 (c 0.05, $CHCl_3$); UV (MeOH) λ_{max} nm: 210, 270; HREIMS *m/z*: 340.1637 ($C_{21}H_{24}O_4$, 340.1675); EIMS *m/z* (%): 340 (M^+, 1), 280 (70), 262 (4), 175 (12), 159 (15), 147 (20), 133 (46), 107 (100), 105 (50), 91(52); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.15–7.27 (5H, m, protons of a mono-substituted benzene ring), 7.00 (2H, d, J = 8.4 Hz, H-2″, 6″), 6.74 (2H, d, J = 8.4 Hz, H-3″, 5″), 5.23 (1H, m, H-5), 2.72–2.88 (6H, m, H-1, 2, 4), 2.48–2.58 (2H, m, H-7), 1.94 (3H, s, $OCOCH_3$), 1.82 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 30.1 (C-1), 45.0 (C-2), 207.3 (C-3), 47.4 (C-4), 70.5 (C-5), 36.9 (C-6), 31.2 (C-7), 142.2 (C-1′), 129.1 (C-2′), 129.1 (C-3′), 126.7 (C-4′), 129.1 (C-5′), 129.1 (C-6′), 132.9 (C-1″), 129.9 (C-2″), 115.9 (C-3″), 156.4 (C-4″), 115.9 (C-5″), 129.9 (C-6″), 170.6 (C=O), 20.9 (CH_3). (5*R*)-5-hydroxy-1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-3-heptanone (**4**), oil, $[\alpha]_{20}^{D}$ − 13.6 (c 0.04, $CHCl_3$); EIMS *m/z*(%): 344 (M^+, 10), 326 (45), 205 (10), 175 (5), 150 (15), 137 (100), 107 (90); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.00 (2H, d, J = 8.4 Hz, H-2′, 6′), 6.79 (1H, d, J = 1.8 Hz, H-2″), 6.74 (1H, d, J = 8.4 Hz, H-5″), 6.71 (2H, d, J = 8.4 Hz, H-3′, 5′), 6.62 (1H, dd, J = 1.8, 8.4 Hz, H-6″), 4.02 (1H, m, H-5), 3.79 (3H, s, OCH3), 2.76 (4H, m, H-1, 2), 2.68 (1H, m, H-7a), 2.60 (2H, m, H-4), 2.50 (1H, m, H-7b), 1.67 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 31.4 (C-1), 45.8 (C-2), 210.3 (C-3), 50.7 (C-4), 67.6 (C-5), 40.0 (C-6), 31.9 (C-7), 133.5 (C-1′), 129.9 (C-2′), 115.8 (C-3′), 156.1 (C-4′), 115.8 (C-5′), 129.9 (C-6′), 134.4 (C-1″), 115.9 (C-2″), 148.0 (C-3″), 145.4 (C-4″), 115.6 (C-5″), 121.4 (C-6″), 56.7 (OCH_3).

(5*R*)-5-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4,5-dihydroxy-3-methoxyphenyl)-3-heptanone (**5**), colourless oil, $[\alpha]_{20}^{D}$ − 19.0 (c0.1, $CDCl_3$); EIMS *m/z* (%): 390 (M^+, 12), 372 (40), 179 (30), 153 (72), 137 (100); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 6.78 (1H, d, J = 1.8 Hz, H-2′), 6.71 (1H, d, J = 7.8 Hz, H-5′), 6.61 (1H, dd, J = 1.8, 7.8 Hz, H-6′), 6.36 (1H, d, J = 1.8 Hz, H-2″), 6.34 (1H, d, J = 1.8 Hz, H-6″), 4.03 (1H, m, H-5), 3.77 (3H, s, OCH_3), 3.75 (3H, s, OCH3), 2.76–2.46 (8H, m, H-1, 2, 4, 7), 1.68 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 30.5 (C-1), 45.8 (C-2), 210.4 (C-3), 50.7 (C-4), 67.6 (C-5), 39.9 (C-6), 32.2 (C-7), 133.5 (C-1′), 112.7 (C-2′), 148.1 (C-3′), 145.4 (C-4′), 115.6 (C-5′), 121.4 (C-6′), 133.9 (C-1″), 104.5 (C-2″), 148.8 (C-3″), 132.5 (C-4″), 145.9 (C-5″), 109.5 (C-6″), 56.3 (OCH_3), 56.1 (OCH_3).

1-Phenyl-7-(4-hydroxy-3-methoxyphenyl)-4*E*-en-3-heptanone (**6**), oil, EIMS *m/z* (%): 310 (M^+, 30), 205 (5), 162 (8), 137 (100), 122 (12), 91 (15); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.15–7.21 (5H, m, protons of a mono-substituted benzene ring), 6.90 (1H, dt, J = 16.2, 6.8 Hz, H-5), 6.83 (1H, d, J = 1.8 Hz, H-2″), 6.74 (1H, d, J = 7.8 Hz, H-5″), 6.55 (1H, dd, J = 1.8, 7.8 Hz, H-6″), 6.10 (1H, d, J = 16.2 Hz, H-4), 3.80 (3H, s, OCH_3), 2.87 (4H, m, H-1, 2), 2.69 (2H, m, H-7), 2.50 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 30.1 (C-1), 41.7 (C-2), 199.3 (C-3), 130.6 (C-4), 146.4 (C-5), 34.4 (C-6), 34.1 (C-7), 141.2 (C-1′), 128.3 (C-2′), 128.4 (C-3′), 126.0 (C-4′), 128.4 (C-5′), 128.3 (C-6′), 132.5 (C-1″), 111.0 (C-2″), 146.5 (C-3″), 144.1 (C-4″), 114.4 (C-5″), 121.5 (C-6″), 55.8 (OCH_3).

1-(4-Hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-4*E*-en-3-heptanone (**7**), oil, EIMS *m/z* (%): 326 (M^+, 50), 175 (5), 137 (100), 205 (15), 150 (10), 107 (95); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.03 (2H, d, J = 8.4 Hz, H-2′, 6′), 6.90 (1H, dt, J = 15.6, 6.7 Hz, H-5), 6.83 (1H, d, J = 1.8 Hz, H-2″), 6.76 (1H, d, J = 8.4 Hz, H-5″), 6.74 (2H, d, J = 8.4 Hz, H-3′, 5′), 6.66 (1H, dd, J = 1.8, 8.4 Hz, H-6″), 6.10 (1H, d, J = 15.6 Hz, H-4), 3.81 (3H, s, OCH_3), 2.82 (4H, m, H-1, 2), 2.70 (2H, m, H-7), 2.50 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 34.2 (C-1), 42.3 (C-2), 199.6 (C-3), 131.4 (C-4), 147.1 (C-5), 35.1 (C-6), 34.7 (C-7), 133.2 (C-1′), 130.0 (C-2′), 115.8 (C-3′), 156.5 (C-4′), 115.8 (C-5′), 130.0 (C-6′), 133.1 (C-1″), 115.9 (C-2″), 145.6 (C-3″), 143.7 (C-4″), 115.6 (C-5″), 121.5 (C-6″), 56.2 (OCH_3).

1-Phenyl-7-(4-hydroxyphenyl)-4*E*-en-3-heptanone (**8**), oil, EIMS *m/z* (%): 280 (M^+, 15), 262 (2), 186 (8), 174 (7), 159 (18), 147 (2), 133 (3), 120 (10), 107 (100), 105 (8), 91 (18); ^1H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.16–7.27 (5H, m, protons of a mono-substituted benzene ring), 7.03 (1H, d, J = 8.4 Hz, H-2″, 6″), 6.90 (1H, dt, J = 16.2, 6.8 Hz, H-5), 6.75 (1H, d, J = 8.4 Hz, H-3″, 5″), 6.10 (1H, d, J = 16.2 Hz, H-4), 2.87 (4H, m, H-1, 2), 2.69 (2H, m, H-7), 2.48 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 30.6 (C-1), 41.9 (C-2), 199.3 (C-3), 131.3 (C-4), 147.2 (C-5), 35.2 (C-6), 34.2 (C-7), 142.4 (C-1′), 129.1 (C-2′), 129.2 (C-3′), 126.6 (C-4′), 129.2 (C-5′), 129.0 (C-6′), 132.5 (C-1″), 130.0 (C-2″), 115.9 (C-3″), 156.5 (C-4″), 115.9 (C-5″), 130.0 (C-6″).

3,6-Furan-7-(4″-hydroxy-3″-methoxyphenyl)-1-phenylheptane (**9**), yellow crystals, mp 70–72 °C; UV (MeOH) λ_{max} nm (log ε): 202 (4.43), 227 (4.10), 279 (3.36); IR (KBr) ν_{max} cm^{-1}: 3550, 2921, 1516,

Table 1
The ^1H (600 MHz) and ^{13}C NMR (150 MHz) data of officinaruminane A (**1**) in $(CD_3)_2CO$.

Position	δ_H	δ_C
1	2.91 (4H, t, J = 7.8 Hz)	30.6
2	3.16 (4H, t, J = 7.8 Hz)	43.6
3	–	202.7
4	–	131.8
5	–	162.0
6	3.25 (4H, t, J = 7.8 Hz)	38.5
7	2.97 (4H, t, J = 7.8 Hz)	36.1
a	8.30 (1H, s)	137.0
Phenyl		
1′	–	142.0 × 2
1″	–	142.4 × 2
2′, 2″,6′,6″	7.16 (4H, d, J = 7.2 Hz)	129.4,129.3, 129.2,129.1
3′,3″,5′,5″	7.24 (4H, t, J = 7.2 Hz)7.21 (4H, t, J = 7.2 Hz)	129.4,129.3, 129.2,129.1
4′, 4″	7.13–7.16 (2H, m)	126.8, 126.7

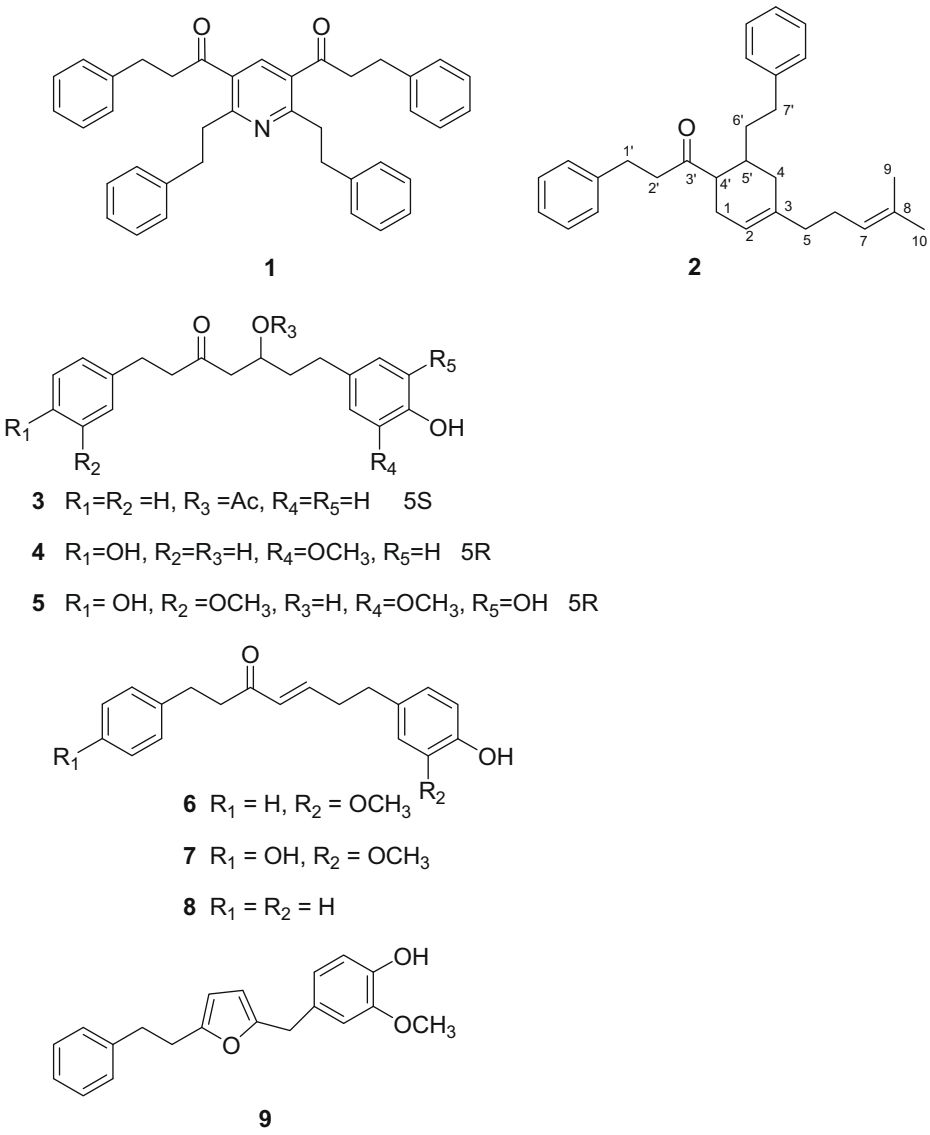

Fig. 1. The structures of compounds **1**–**9**.

1456, 1271, 1238; EIMS *m/z* (%): 308 (M^+, 50), 279 (1), 217 (100), 202 (5), 185 (15), 137 (20), 91 (20); ^{1}H NMR [$(CD_3)_2CO$, 600 MHz) δ: 7.17–7.21 (5H, m, protons of a mono-substituted benzene ring), 6.85 (1H, d, J = 1.8 Hz, H-2′), 6.76 (1H, d, J = 7.8 Hz, H-5″), 6.68 (1H, dd, J = 1.8, 7.8 Hz, H-6″), 5.90 (2H, s, H-3, 4), 3.83 (2H, s, H-1), 3.81 (3H, s, OCH_3), 2.92 (2H, m, H-7), 2.86 (2H, m, H-6); ^{13}C NMR [$(CD_3)_2CO$, 150 MHz] δ: 34.4 (C-1), 154.3 (C-2), 107.2 (C-3), 106.6 (C-4), 154.7 (C-5), 30.5 (C-6), 34.9 (C-7), 130.7 (C-1′), 113.2 (C-2′), 148.2 (C-3′), 145.9 (C-4′), 115.6 (C-5′), 121.8 (C-6′), 142.1(C-1″), 129.0 (C-2″), 129.1 (C-3″), 126.7 (C-4″), 129.1 (C-5″), 129.0 (C-6″), 56.2 (OCH_3).

3. Results and discussion

Dried rhizomes of *A. officinarum* Hance were extracted with 95% EtOH. The EtOH extract was extracted with petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH, respectively. The $CHCl_3$ extract was separated by repeated column chromatography to give three new diarylheptanoids (**1**–**3**, Fig. 1), together with six known analogues (**4**–**9**). The known diarylheptanoids were readily identified as (5*R*)-5-hydroxy-1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-3-heptanone (**4**) (Shin et al., 2002), (5*R*)-5-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4,5-dihydroxy-3-methoxyphenyl)-3-heptanone (**5**) (Ma, Jin, Yang, & Liu, 2004), 1-phenyl-7-(4-hydroxy-3-methoxy phenyl)-4*E*-en-3-heptanone (**6**) (Itokawa, Morita, & Mihashi, 1981), 1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-4*E*-en-3-heptanone (**7**) (Lee et al., 2002), 1-phenyl-7-(4-hydroxy-phenyl)-4*E*-en-3-heptanone (**8**) (Itokawa, Morita, Midorikawa, Aiyama, & Morita, 1985), 3,6-furan-7-(4″-hydroxy-3″-methoxy-phenyl)-1-phenylheptane (**9**) (Sun et al., 2008), by comparison of

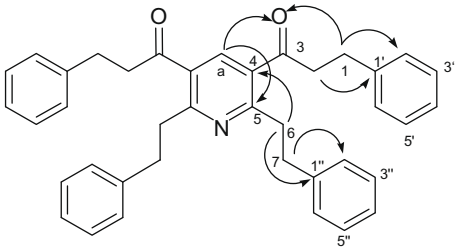

Fig. 2. Key HMBC correlations of **1**.

their physical and spectroscopic data with those reported in the literature.

Officinaruminane A (**1**) was obtained as a colourless oil. Its molecular formula of $C_{39}H_{37}O_2N$ was determined by HREI-MS at *m/z* 551.2823 [M$^+$] (calcd. 551.2824), suggesting the presence of 22 degrees of unsaturation. The EI-MS displayed five key fragment ions at *m/z* 460 (M-91), 446 (M-105), 418 (M-133), 105, and 91. The ^{1}H and ^{13}C NMR spectra of 1 (Table 1) indicated the feature of a diarylheptanoid analogue. Analysis of the ^{1}H NMR, ^{13}C NMR, and HMQC spectroscopic data of **1** revealed 1 the presence of two diarylheptane moieties including four mono-substituted benzene rings (δ_C 142.4 × 2, 142.0 × 2, 129.4 × 4, 129.3 × 4, 129.2 × 4, 129.1 × 4, 126.8 × 2, 126.7 × 2), eight methylene units (δ_C 30.6 × 2, 36.1 × 2, 38.5 × 2, 43.6 × 2), four quaternary carbons (δ_C 131.8 × 2, 162.0 × 2) and two carbonyl carbons (δ_C 202.7), indicating the symmetric property of molecule. The HMBC correlations (Fig. 2) were observed between the methylene protons at δ_H 2.91 (H-1) and the aromatic carbons at δ_C 129.0 (C-2′, 6′) and carbonyl carbon at δ_C 202.7 (C-3), between the methylene protons at δ_H 3.16 (H-2) and the aromatic carbon at δ_C 142.1 (C-1′), between the methylene protons at δ_H 3.25 (H-6) and the aromatic carbons at δ_C 142.4 (C-1″), and between δ_H 2.97 (H-7) and δ_C 162.0 (C-5) and δ_C 129.1(C-2″, 6″). The remaining aromatic proton at δ_H 8.30 (s) in the ^{1}H NMR spectrum and the aromatic carbon at δ_C 137.0 together with the molecular formula suggested the presence of a nitrogen heterocyclic system in the molecule of **1**. The strong long-range correlations of H-a (δ_H 8.30) with carbonyl carbon and C-3 (δ_C 202.7) and C-5 (δ_C 162.0), indicated that a 1,2,4,5-tetrasubstituted pyridine ring was formed by the C-4 and C-5 of two diarylheptanoid moieties, C-a (δ_C 137.0) and a nitrogen atom. Therefore, **1** was elucidated as 2,6-diphenethyl-3,5-di-(3-phenylpropanoyl)-pyridine. To our knowledge, this is the first alkaloid of bi-diarylheptanoids connecting by a pyridine ring.

Officinarumin B (**2**) was obtained as a colourless oil and the molecular formula of $C_{29}H_{36}O$ was determined by HREI-MS at *m/z* 400.2767 [M$^+$] (400.2766), requiring 12 degrees of unsaturation. The EI-MS of **2** displayed a molecular ion at *m/z* 400 and five important fragment ions at *m/z* 331 (M-69), 295 (M-105), 276 (M-133), 133, 105 and 91. The presence of a 1,7-diphenyl-3-heptanone moiety was disclosed by analysis of ^{1}H NMR, ^{13}C NMR (Table 2), HMQC and HMBC spectra data, which showed the signals for two mono-substituted benzene rings (δ_C 126.4, 126.6, 129.2 × 2, 129.1 × 6, 142.5, 143.2), four methylene units, two methyne units and a carbonyl carbon (δ_C 213.5).

The remaining 10 carbon signals are two methyls at δ_C 17.7and 25.8, four olefinic carbons at δ_C 119.5, 125.0, 131.7 and 137.3, and four methylene units at δ_C 38.2, 33.7, 28.5, 27.0, suggesting a feature of a monoterpene subunit. The ^{1}H NMR showed two methyls at δ_H1.58 (3H, br.s, H_3-9) and 1.64 (3H, br.s, H_3-10), which coupled with the olefinic proton at δ_H 5.08 (1H, t, *J* = 6.6 Hz, H-7) in the ^{1}H–^{1}H COSY spectrum. The latter showed a ^{1}H–^{1}H correlation with the methylene protons at δ_H 2.08 (2H, m, H-6), which in turn coupled with the methylene protons at δ_H 1.94 (2H, m, H-5). Another olefinic proton was observed at δ_H 5.35 (1H, br.s, H-2) in the ^{1}H NMR spectrum. The HMBC correlations between H-2 and the methylene carbon (C-5) and between H_2-5 and olefinic carbon (C-2) led to the connection of C-5 to C-3. Analysis of the ^{1}H–^{1}H COSY NMR data led to the identification of the proton spin-systems shown in Fig. 3, which indicated that the monoterpene unit and 1,7-diphenyl-3-heptanone moiety were joined together by forming a cyclohexene ring. The HMBC correlations of H-1 and H-5 with the carbonyl carbon also supported the above conclusions. Thus, **2** was identified as 1-(4-(4-methylpent-3-enyl)-6-phenethylcyclohex-3-enyl)-3-phenylpropan-1-one, an unusual diarylheptanoid coupled with a monoterpene unit.

Compound **3** was obtained as a colourless oil with $[\alpha]_{20}^{D}$ + 5.45° (c 0.05, $CHCl_3$). The molecular formula of $C_{21}H_{24}O_4$ was determined by HREI-MS at *m/z* 340.1673 [M$^+$] (340.1675), suggesting the presence of 10 degrees of unsaturation. Analysis of the ^{1}H NMR, ^{13}C NMR, and HMQC data of **3** revealed the characteristic of diarylheptanoids, including a mono-substituted benzene ring, a 1, 4-disubstituted benzene ring, five methylene units, an oxygenated methyne unit and a ketone carbonyl group. The ^{1}H NMR spectrum of **3** displayed five aromatic protons from a mono-substituted benzene ring at δ_H 7.13–7.25 (10H, m), four aromatic protons from a 1, 4-disubstituted benzene ring at δ_H 7.00 (2H, d, *J* = 8.4 Hz, H-2″, 6″), 6.74 (2H, d, *J* = 8.4 Hz, H-3″, 5″), an oxygenated methyne proton at δ_H 5.23 (1H, m, H-5), five methylene protons at δ_H 2.72–2.88 (6H, m, H-1, 2, 4), 2.48–2.58 (2H, m, H-7), 1.82 (2H, m, H-6). In the ^{1}H–^{1}H COSY experiment, H-5 was coupled with H-6, whereas the latter were also coupled with H-7. The long-range correlations between H-5 and the carbonyl carbon at δ_C 207.3 (C-3), H-6 and C-1″ (δ_C 132.9), H-7 and C-2″, 6″ in the HMBC spectrum (Fig. 4) confirmed the connection of a 1, 4-disubstituted benzene ring with C-7. The presence of an acetyl group in the heptanone chain was deduced from the proton signal at δ_H 1.94 (3H, s) and the carbons at δ_C 170.6 and 20.6. The locations of the acetyl group at C-5 were determined by the long range correlations between H-5 and the ester carbonyl carbon in the HMBC spectrum. The absolute stereo-

Table 2
The ^{1}H (600 MHz) and ^{13}C NMR (150 MHz) data of officinaruminane B (**2**) in $(CD_3)_2CO$.

Position	δ_H	δ_C
1	2.00 (1H, m), 2.15 (1H, m)	28.5
2	5.35 (1H, br.s)	119.5
3	–	137.3
4	1.77 (1H, m), 2.20 (1H, m)	33.7
5	1.94 (2H, m)	38.2
6	2.08 (2H, m)	27.0
7	5.86 (1H, t, *J* = 6.6 Hz)	125.0
8	–	131.7
9	1.64 (3H, s)	25.8
10	1.58 (3H, s)	17.7
1′	2.80 (2H, m)	30.1
2′	2.80 (2H, m)	40.2
3′	–	213.5
4′	2.52 (1H, m)	52.5
5′	1.92 (1H, m)	35.5
6′	1.42 (1H, m), 1.64 (1H, m)	36.6
7′	2.52 (1H, m), 2.69 (1H, m)	33.5
Phenyl		
1″		142.5
1‴		143.2
2″, 6″, 2‴, 6‴	7.14 (2H, m)7.19 (2H, t, *J* = 7.8 Hz	129.2, 129.2, 129.1,129.1,
3″,5″, 3‴″,5‴″	7.23 (2H, t, *J* = 7.8 Hz)7.22(2H, t, *J* = 7.8 Hz)	129.1,129.1, 129.1,129.1
4″, 4‴″	7.13 (2H, m)	126.6, 126.4

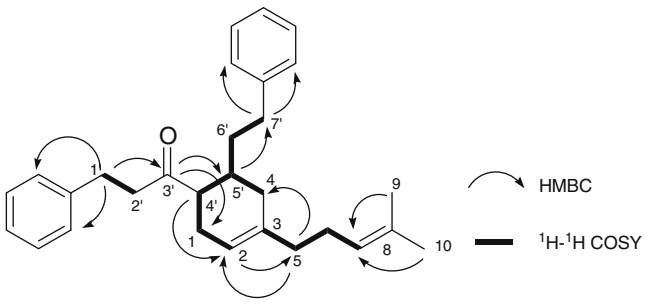

Fig. 3. HMBC and ^{1}H–^{1}HCOSY correlations of **2**.

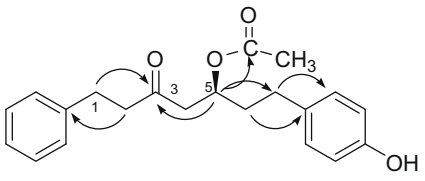

Fig. 4. HMBC correlations of **3**.

chemistry of **3** at C-5 was determined to be *S* based on its positive optical rotation at +5.45, the negative optical rotation indicating the 5*R* configuration (An et al., 2008). Accordingly, compound **3** was assigned as 5(S)-acetoxy-7-(4-dihydroxyphenyl)-1-phenyl-3-heptanone.

Acknowledgements

The authors would like to thank Mr. He-Bin Chen and Ms. Yan Xie, Instrumental Analysis Center of the Academy of Military Medical Sciences, China, for NMR and MS measurements, respectively.

References

Ali, M. S., Tezuka, Y., Banskota, A. H., & Kadota, S. (2001). Blepharocalyxins C–E, three new dimeric diarylheptanoids, and related compounds from the seeds of *Alpinia blepharocalyx*. *Journal of Natural Products, 64*, 491–496.

An, N., Xu, L.-Z., Zou, Z.-M., & Yang, S.-L. (2006). Diarylheptanoids from *Alpinia officinarum*. *Journal of Asian Natural Products Research, 8*, 637–641.

An, N., Zou, Z. M., Tian, Z., Luo, X. Z., Yang, S. L., & Xu, L. Z. (2008). Diarylheptanoids from the rhizomes of *Alpinia officinarum* and their anticancer activity. *Fitoterapia, 79*, 27–31.

Doug, H., Chen, S. X., Xu, H. X., Kadota, S., & Namba, T. (1998). A new antiplatelet diarylheptanoid from *Alpinia blepharocalyx*. *Journal of Natural Products, 61*, 142–144.

Fan, G. J., Kang, Y. H., Han, Y. N., & Han, B. H. (2007). Platelet-activating factor (PAF) receptor binding antagonists from *Alpinia officinarum*. *Bioorganic and Medicinal Chemistry Letters, 17*, 6720–6722.

Hikino, H., Kiso, Y., Kato, N., Hamada, Y., Shioiri, T., Aiyama, R., Itokawa, H., Kiuchi, F., & Sankawa, U. (1985). Antihepatotoxic actions of gingerols and diarylheptanoids. *Journal of Ethnopharmacology, 14*, 31–39.

Itokawa, H., Morita, H., Midorikawa, I., Aiyama, A. R., & Morita, M. (1985). Diarylheptanoids from the rhizome of *Alpinia officinarum* Hance. *Chemical and Pharmaceutical Bulletin, 33*, 4889–4893.

Itokawa, H., Morita, M., & Mihashi, S. (1981). Two new diarylheptanoids from *Alpinia officinarum* Hance. *Chemical and Pharmaceutical Bulletin, 29*, 2383–2385.

Jiangsu New Medicinal College (1979). *The dictionary of Chinese herbal medicines* (p. 1902). Shanghai: Shanghai People's Publishing Press.

Kim, Y.-U., Son, H. K., Song, H. K., Ahn, M.-J., Lee, S. S., & Lee, S. K. (2003). Inhibition of 5<alpha>-reductase activity by diarylheptanoids from *Alpinia officinarum*. *Planta Medica, 69*, 72–74.

Lee, H. J., Kim, J. S., & Ryu, J. H. (2006). Suppression of inducible nitric oxide synthase expression by diarylheptanoids from *Alpinia officinarum*. *Planta Medica, 72*, 68–71.

Lee, K. S., Li, G., Kim, S. H., Lee, C. S., Woo, M. H., Lee, S. H., Jhang, Y. D., & Son, J. K. (2002). Cytotoxic diarylheptanoids from the roots of *Juglans mandshurica*. *Journal of Natural Products, 65*, 1707–1708.

Ma, J., Jin, X., Yang, L., & Liu, Z. L. (2004). Diarylheptanoids from the rhizomes of *Zingiber officinale*. *Phytochemistry, 65*, 1137–1143.

Shin, J.-E., Han, M. J., Song, M.-C., Baek, N.-I., & Kim, D.-H. (2004). 5-Hydroxy-7-(4′-hydroxy-3′-methoxyphenyl)-1-phenyl-3-heptanone: A pancreatic lipase inhibitor isolated from *Alpinia officinarum*. *Biological and Pharmaceutical Bulletin, 27*, 138–140.

Shin, D., Kinoshita, K., Koyama, K., & Takahashi, K. (2002). Antiemetic principles of *Alpinia officinarum*. *Journal of Natural Products, 65*, 1315–1318.

Sun, Y., Tabata, K., Matsubara, H., Kitanaka, S., Suzuki, T., & Yasukawa, K. (2008). New cytotoxic diarylheptanoids from the rhizomes of *Alpinia officinarum*. *Planta Medica, 74*, 427–431.

Yao, H., Zhou, G. X., Wu, Q., Lei, G. Q., Chen, D. F., Chen, J. K., & Zhou, T. S. (2007). Mistletonone, a novel antioxidative diarylheptanoid from the branches and leaves of *Viscum coloratum*. *Molecules, 12*, 312–317.